

TRANSLATION

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(54) Title:
**Dyeing of Multicolor Effects on Polyamide Fiber Materials in the
Presence of Manganese Compounds**

(57) Abstract

The invention pertains to a process for the dyeing of polyamide fiber mixtures which contain regularly stainable polyamide fiber materials and acid-modified polyamide fiber materials, with dye mixtures of acid dyes and cationic dyes, characterized in that before, during, or after the dyeing, at least one manganese(II) compound is added to the bath. The dyed materials obtained in this way show good light fastness.

Specification

The present invention pertains to a process for achieving multicolored effects on mixtures of different dyeable polyamide fiber materials in the presence of manganese compounds, which yields dyed materials with improved light fastness, and the polyamide fiber material treated with this.

Polyamide fiber materials are thermally and/or photochemically sensitive. The polyamide fiber can be damaged by the influence of light and/or heat.

For many applications it is necessary to give the polyamide fiber material a matte surface appearance, which is achieved industrially by introducing titanium dioxide pigments. Polyamide fiber materials pigmented in this way have proved particularly sensitive.

The goal of the present invention is to reduce the thermal and/or photochemical instability of polyamide fiber materials to achieve high light fastness, good care resistance, and aging resistance.

It has now been found that by dyeing polyamide fiber mixtures that consist of regularly dyeable polyamide fiber materials and acid-modified polyamide fiber material with dye mixtures of acid dyes and cationic dyes in the presence of manganese(II) compounds, thermal and/or photochemical instability can be eliminated completely or at least to a great extent and improved light fastness is achieved.

Therefore the invention pertains to a process for the dyeing of polyamide fiber mixtures that contain regularly dyeable polyamide fiber materials and acid-modified polyamide fiber materials with dye mixtures of acid dyes and cationic dyes, which is characterized in that before, during, and after the dyeing, at least one manganese(II) compound is added to the bath.

Surprisingly the dyed materials obtained with the process in accordance with the invention show improved light fastness and improved tear resistance.

As manganese(II) compounds in the process in accordance with the invention, all inorganic and organic salts as well as Mn(II) complex compounds come under consideration. The following may be mentioned as examples of inorganic salts: chlorides, acetates, phosphates, nitrates, and sulfates. The following may be mentioned as examples of organic salts: formates, oxalates, and lactates. Examples of Mn(II) complex compounds may

include: Mn(II) complexes of citric acid, ethylenediaminetetraacetic acid, or phosphono-alkane-polycarboxylic acids.

The Mn(II) compounds mentioned may also be used in arbitrary mixtures with one another.

The Mn(II) compounds may be added to the dye bath before, during, or after the dyeing process.

It has proven particularly advantageous to add the Mn(II) compounds to the dye bath during the dyeing process. The Mn(II) compounds are advantageously added to the dye bath in quantities of 0.01 to 5 g/l, especially 0.1 to 1 g/l, preferably 0.1 to 0.7 g/l.

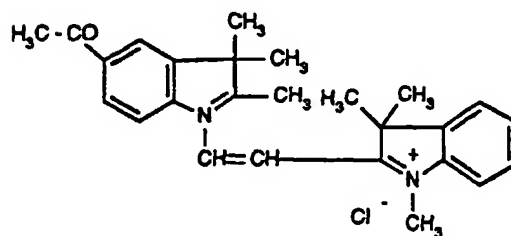
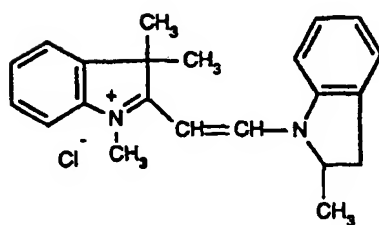
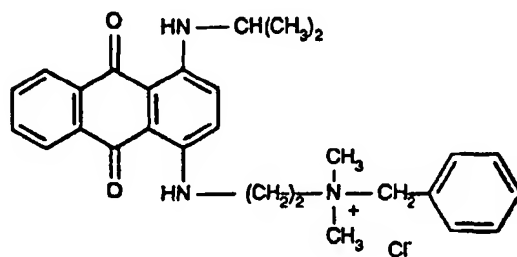
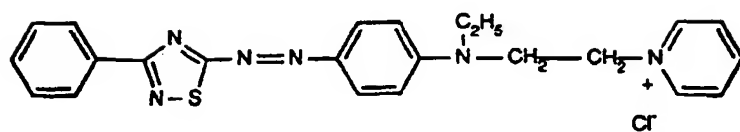
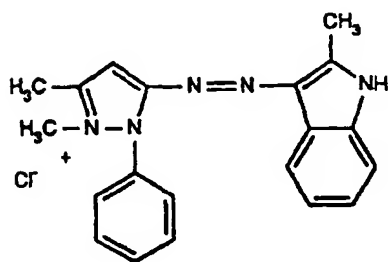
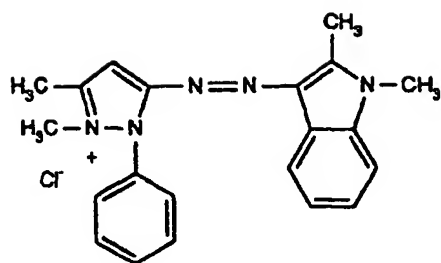
For the process in accordance with the invention, as acid dyes for example the dyes specified in the *Colour Index*, Third Edition of 1971, vol. 1, under C.I. Acid Dyes on pages 1003 to 1561 and in the supplements to this are suitable.

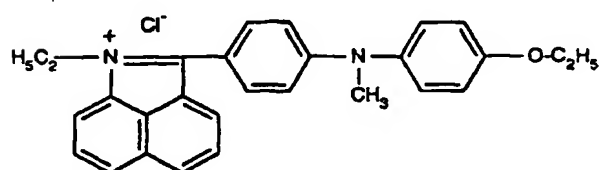
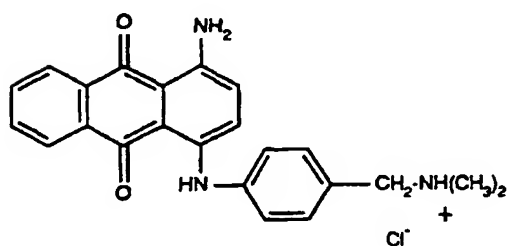
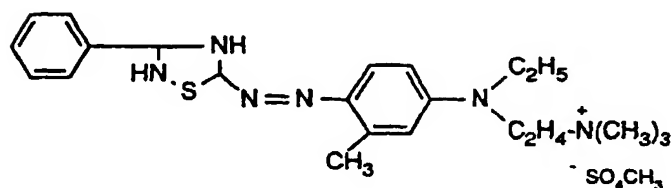
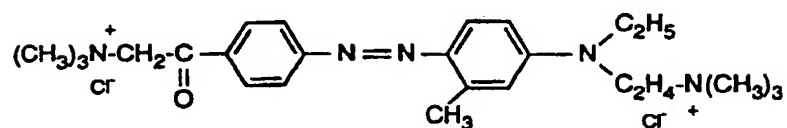
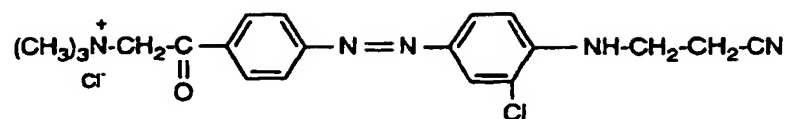
For the process in accordance with the invention as cationic dyes for example those dyes listed in the *Colour Index*, Third Edition of 1971, vol. 1, under C.I. Basic Dyes on pages 1611 to 1688 and in the supplements are suitable.

The acid dyes and the cationic dyes that are used in the process in accordance with the invention are known and can be produced according to known methods.

Chemically, the cationic dyes are dyes that have a colored (chromophor-containing) cation, especially a quaternary nitrogen atom, and a colorless anion. The dyes are present in the form of a salt of an inorganic or organic acid. They belong to a great variety of chemical classes; for example this may involve sulfates, chlorides, acetates, or methylsulfates of azo dyes, such as monoazo-, disazo-, and polyazo dyes; anthraquinone dyes; phthalocyanine dyes, diphenylmethane and triarylmethane dyes, methane, polymethine, azomethine, and azacyanine dyes; thiazole, ketonimine, acridine, cyanine, nitro, quinoline, benzimidazole, xanthene, azine, oxazine, and thiazine dyes. Preferred cationic dyes are those that contain a quaternary nitrogen atom in a heterocyclic ring; however, cationic dyes may also be used which contain the quaternary nitrogen atom on an alkyl chain.

As examples of cationic dyes that can be used in the process in accordance with the invention, the following come under consideration:



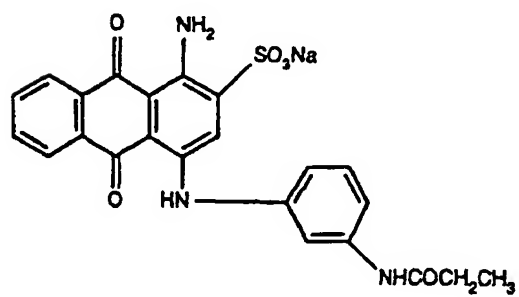
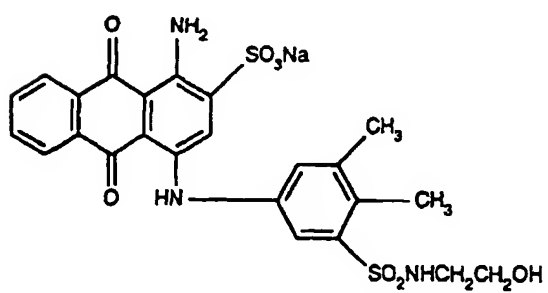
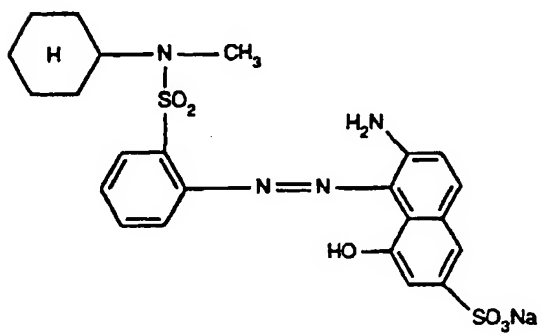
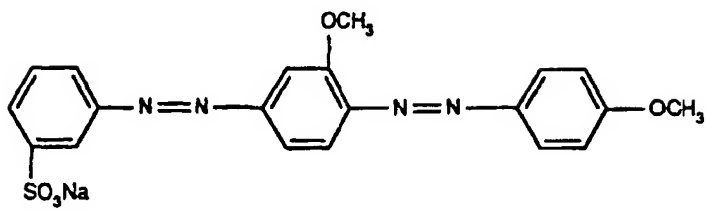
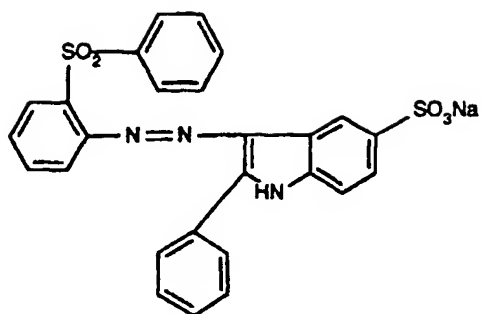


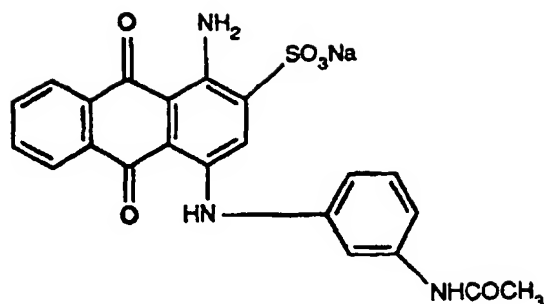
The acid dyes involve water-soluble dyes, which usually contain one or more water-solubilizing groups, especially sulfonic acid groups.

The acid dyes generally exist in the form of salts. As salts, especially alkali salts, particularly sodium, potassium, or lithium salts, and ammonium-containing salts, for example, ammonium or tetraalkylammonium salts, come under consideration.

The acid dyes can belong to a great variety of classes, for example azo dyes, such as monoazo-, disazo-, and polyazo dyes; anthraquinone dyes, phthalocyanine dyes, diphenylmethane and triarylmethane dyes; methane, polymethine, and azomethine dyes.

As examples of acid dyes that can be used in the process in accordance with the invention, for example, the following come under consideration:



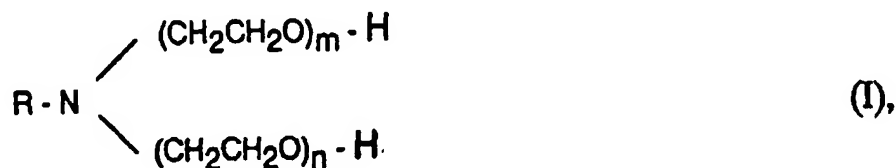


The dyeing in accordance with the process of the invention generally takes place under the conditions for dyeings on synthetic polyamide with cationic dyes and acid dyes. A temperature between 30 and 130°C, especially between 50 and 98°C, has proven suitable as the dyeing temperature. The pH is usually between 3.5 and 7.0, wherein it is particularly advantageous to modify the pH during dyeing in the direction of acid pH.

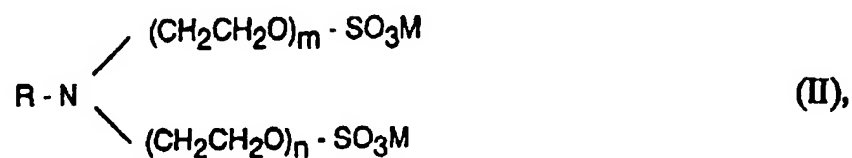
A preferred embodiment of the process in accordance with the invention is characterized in that a complexing agent that can form a complex with the Mn^{2+} ions is added to the dye bath. As complexing agent, the following compounds have proven suitable: gluconic acid, polyaminopolycarboxylic acid, tripolyphosphates, orthophosphates, phosphonic acid, phosphonoalkanepolycarboxylic acids, citric acid, ethylenediaminetetraacetic acid.

Likewise preferred is an embodiment of the process in accordance with the invention which is characterized in that a balancing agent is added to the dye bath. As the balancing agent, for example, commercial balancing agents come under consideration, as are suggested for example in EP-A-0 089 004.

Preferably the following compounds are used as balancing agents: compounds of the formula

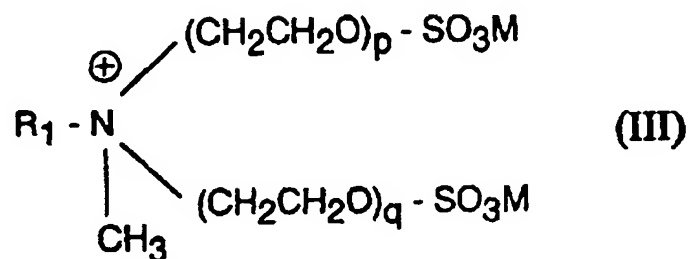


wherein R represents C₈-C₂₂-alkyl, C₈-C₂₂-alkenyl or C₈-C₂₂-cycloalkenyl; especially R-N is the tallow fatty amine radical, and m+n is 2 to 25, especially 2 to 15; or the formula



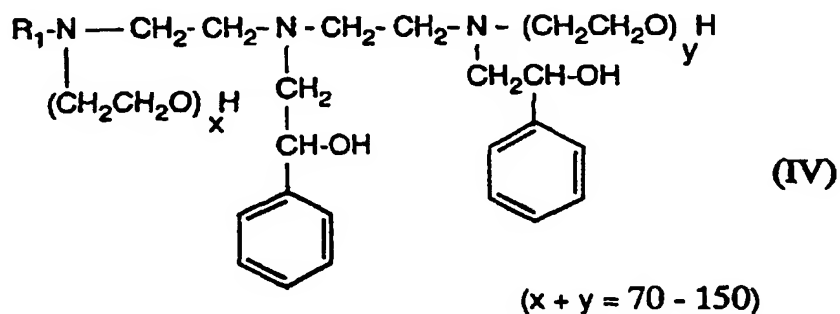
wherein R represents C₈-C₂₂-alkyl, C₈-C₂₂-alkenyl or C₈-C₂₂-cycloalkenyl, in particular R-N is the radical of tallow fatty amine, m+n is 2 to 25, especially 2 to 15, and M is hydrogen, alkali metal or ammonium;

Compounds of the formula

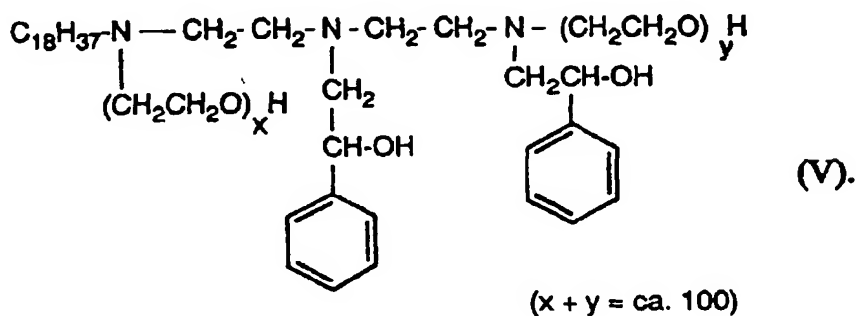


wherein R₁ represents C₈-C₂₂-alkyl, C₈-C₂₂-alkenyl or C₈-C₂₂-cycloalkenyl, especially a C₂₀-C₂₂-hydrocarbon radical and p+q = 15 – 60, especially 20 – 40, preferably 34, and M is hydrogen, alkali metal or ammonium;

Compounds of the formula



wherein R₁ represents C₈-C₂₂-alkyl, C₈-C₂₂-alkenyl or C₈-C₂₂-cycloalkenyl, especially compounds of the formula



In addition, mixtures of the components mentioned are also significant as balancing agents. The dye bath can also contain additional customary auxiliaries, for example wetting agents, deaerating agents, and/or antifoam agents, etc.

The application of the manganese(II) compounds can take place continuously or batchwise.

In the process in accordance with the invention, carpets are preferably made of mixtures of acid-modified polyamide fiber material and regular polyamide fiber material, wherein the latter can be used in various deep-dyeable types.

The dyeing process takes place in a manner known in and of itself.

In dyeing according to the extraction process, the bath ratio can be selected within a broad range, e.g. 1:2 to 1:100, preferably 1:10 to 1:40. It is advantageous to work at a temperature of 30 to 130°C, preferably 50 to 98°C.

In dyeing according to the continuous process, the bath application rate advantageously amounts to 40 to 700, preferably 40 to 500 percent by weight, followed by a steaming process, e.g. at 100°C for 5 minutes.

After the end of the dyeing process, the dyed products produced are washed and dried in the usual way.

According to the present invention, dyed materials with good thermal and/or photochemical stability are obtained.

As dyes to be stabilized in accordance with the invention, those come under consideration which are produced from acid dyes and cationic dyes, especially axo and anthraquinone dyes.

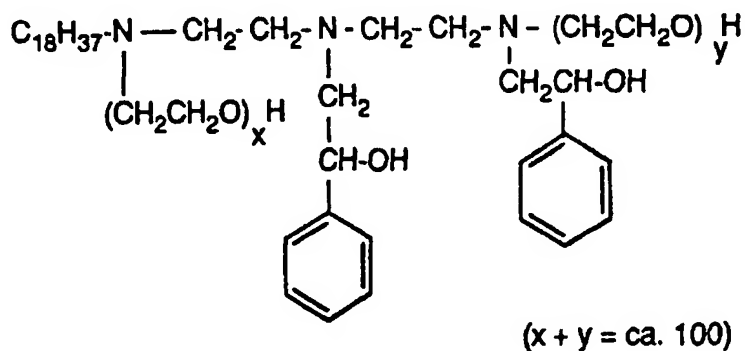
Polyamide fiber material in the process according to the invention is defined as a mixture of synthetic polyamide material, especially polyamide-6 or polyamide-66 in a mixture with acid-modified polyamide fiber material, i.e., basically dyeable polyamides. Fundamentally the polyamide material can exist in a great variety of processing forms, for example as fibers, yarn, woven materials, knitted materials, nonwoven materials, or floc materials. Polyamide carpets are preferred. The polyamide fiber material made of regular and acid-modified polyamide can exist in any desired mixing ratio. Mixtures of these polyamide fiber materials in a 10:1 to 1:10 ratio, especially 25:75 to 75:25 and advantageously 40:60 to 60:40, are preferred.

The examples that follow will illustrate the invention. "Parts" means parts by weight and "percent" means percent by weight. Temperatures are given in degrees Celsius. The percent by weight values given pertain to the fiber weight used.

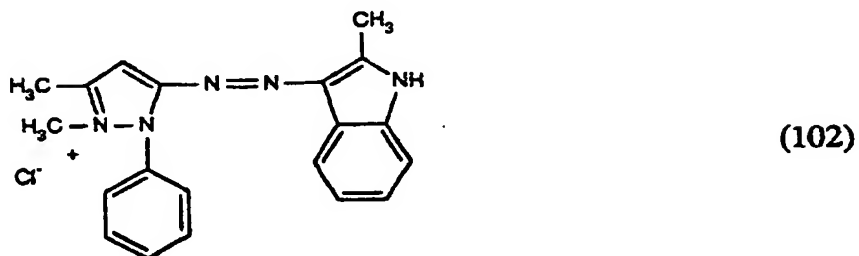
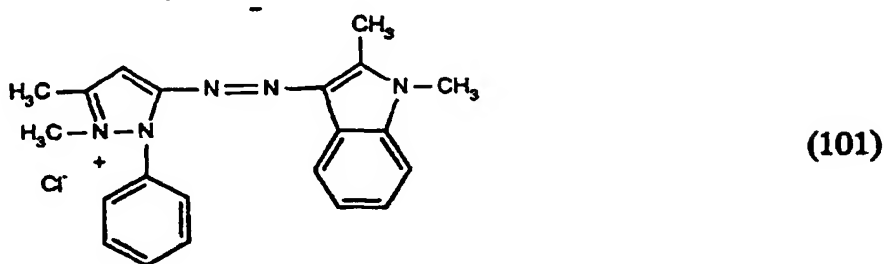
Example 1:

Two samples, 20 g each, of a prewashed polyamide carpet are prepared; the pile has a weight of 500 g/m² and consists of 50 wt % regularly dyeable polyamide fiber material and 50 wt % basically dyeable polyamide fiber material of 1300 dtex. These samples are dyed in bombs [for example in a Labomat® from the firm of Mathis, Niederhasli, Switzerland], wherein the bath ratio is 1:25. For both dyeings, first a bath of the following composition is prepared:

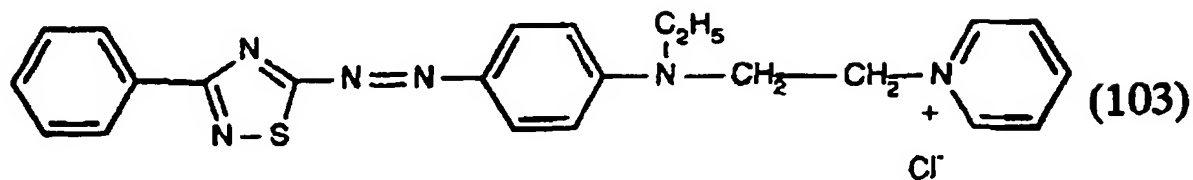
1 g/l of the dye auxiliary of the formula



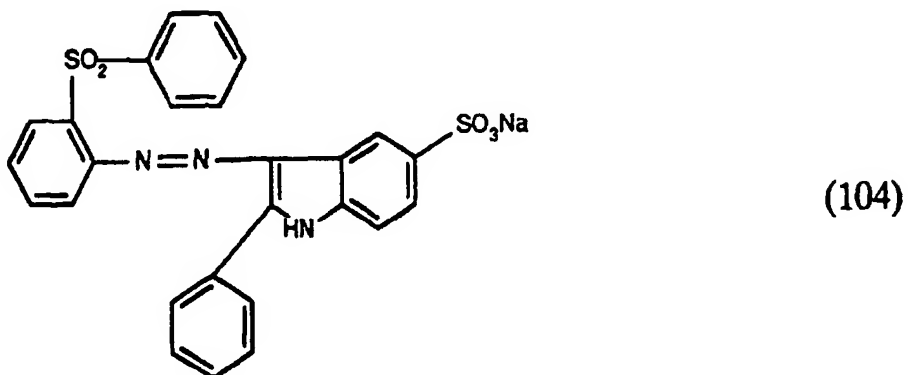
and 1 wt % acetic acid (80%). The following dyes are dissolved in the baths: 0.05 wt % of a 1:1 mixture of the dyes of the formulas



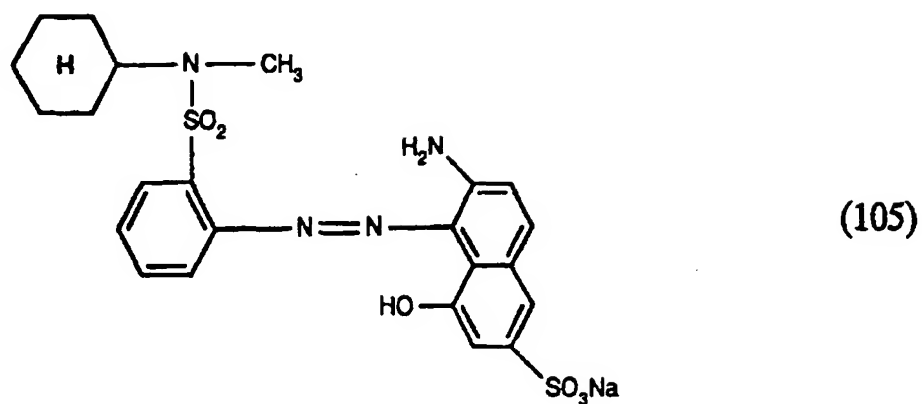
0.15 wt % of the dye of the formula



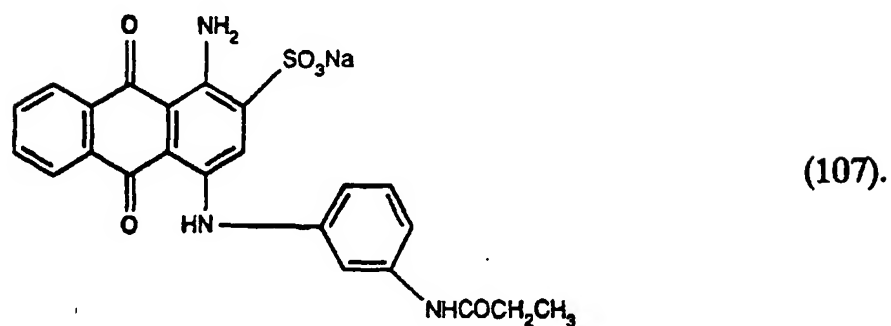
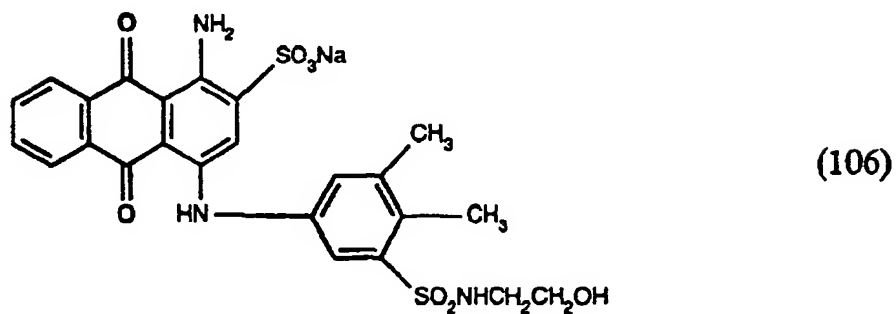
0.04 wt % of the dye of the formula



0.05 wt % of the dye of the formula



and 0.15 wt % of the 3:1-mixture of the dyes of the formulas



The bath is separated into two portions. Bath 1 remains unchanged, but on the other hand bath 2 is treated with 0.5 g/l manganese(II) acetate.

The carpet samples are placed in the baths, heated to 40°C, and the dyeing is begun.

First, heating is performed at a rate of 2°C/min to 95°C, then the dyeing is performed for 60

minutes at this temperature, followed by cooling, cold rinsing, centrifugation, and drying at 100°C.

The product is a carpet with an orange/blue pattern. The separation of the two colors is excellent on both samples.

The light fastness is determined for the two samples according to ISO standard 105-B02 and AATCC 16E. The following results are obtained:

Carpet dyed with	Light fastness ISO 105-B02 after 300 hours	Light fastness AATCC 16E after 150 hours
Dye bath 1	5	3
Dye bath 2	6 - 7	3 - 4

The light fastness readings according to ISO 105-B02 are determined with the blue scale, and the light fastness readings according to AATCC 16E are determined with the gray scale.

It is apparent from the illuminated patterns that the improvement of the light fastness particularly pertains to the basically dyeable part, since this dominates the design because of its color (orange).

Addition of Mn(II) ions brings about an improvement of the light fastness.

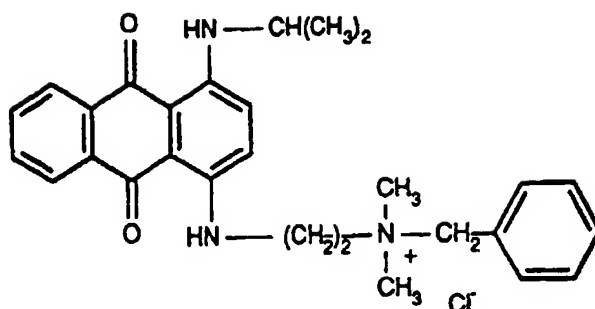
Example 2:

20 g of a prewashed polyamide carpet are prepared, the nap of which consists of fibers dyeable with basic and acid dyes in a 1:1 ratio. The dyeing is performed as in example 1, but the following dye combination is used:

0.002 wt % of the 1:1 dye mixture of the dyes of formulas (101) and (102),

0.01 wt % of the dye of formula (103),

0.04 wt % of the dye of formula



(108),

0.22 wt % of the dye of formula (104),

0.18 wt % of the dye of formula (105) and,

0.26 wt % of the 3:1 dye mixtures of the dyes of formulas (106) and (107).

The dye bath 3 remains analogous to dye bath 1 without addition of Mn(II) ions, whereas 3 wt % of the following compound are added to dye bath 4: Mn(II) complex of the tetrasodium salt of ethylenediamine tetraacetic acid.

The preparation and drying of the dyed material takes place as indicated in example 1.

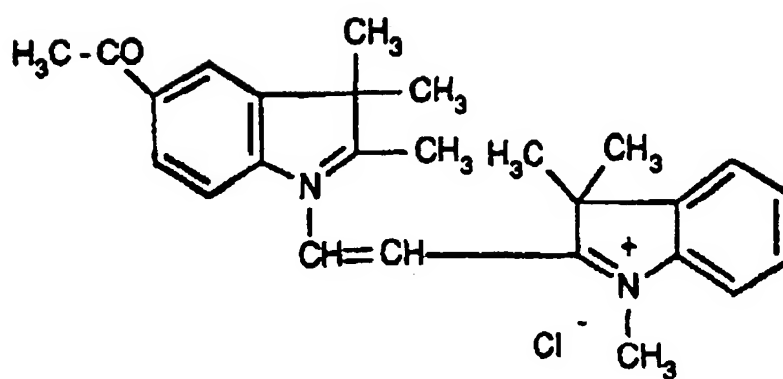
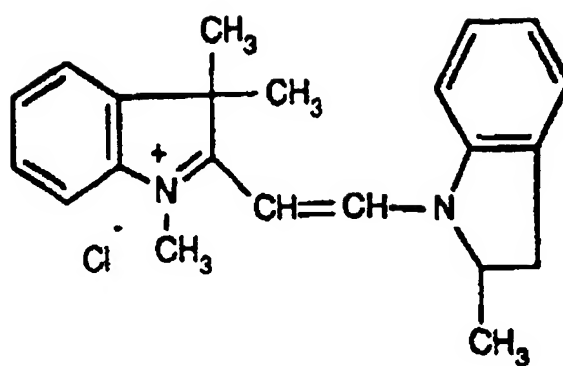
The determination of the light fastness of the two samples takes place according to ISO standard 105-B02 and AATCC 16E. The following results are obtained:

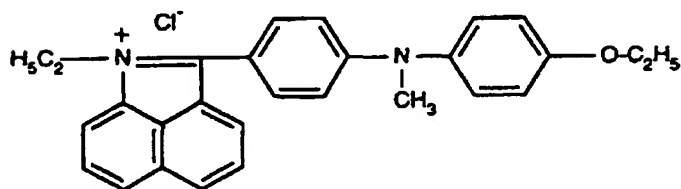
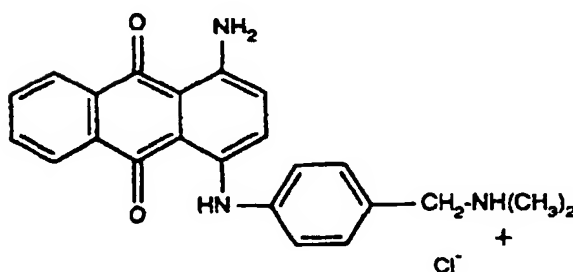
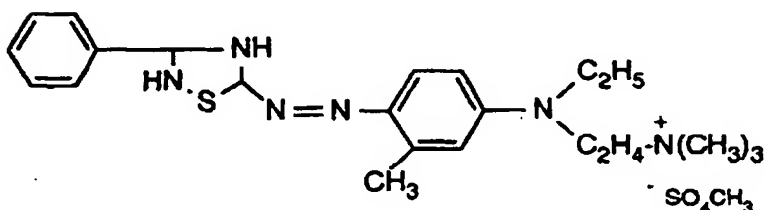
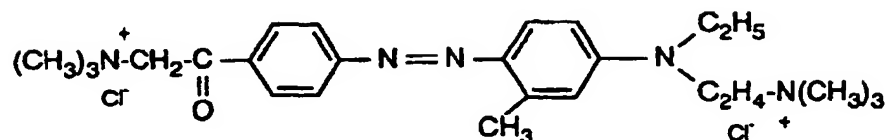
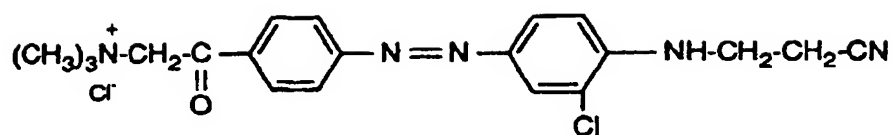
Dyeing with	Light fastness ISO 105-B02 after 300 hours	Light fastness AATCC 16E after 150 hours
Dye bath 3	4 – 5	3
Dye bath 4	6	4

The light fastness readings according to ISO 105-B02 are determined with the blue scale and the light fastness readings according to AATCC 16E are determined with the gray scale.

It is apparent from the illuminated patterns that the improvement pertains exclusively to the basically dyeable portion.

If the procedures specified in examples 1 and 2 are followed, and instead of the dyes indicated there, those of the following formulas are used, dyed materials with improved light fastness are likewise obtained:





Claims

1. Process for dyeing polyamide fiber mixtures that contain regularly dyeable polyamide fiber materials and acid-modified polyamide fiber materials, with dye mixtures of acid dyes and cationic dyes, characterized in that before, during, or after dyeing, at least one manganese(II) compound is added to the bath.
2. Process in accordance with claim 1, characterized in that inorganic or organic salts or Mn(II) complex compounds are used as the manganese(II) compounds.

3. Process in accordance with claim 2, characterized in that manganese chlorides, acetates, phosphates, nitrates or sulfates are used.
4. Process in accordance with claim 2, characterized in that manganese formates, oxylates, or lactates are used.
5. Process in accordance with claim 2, characterized in that as the manganese(II) complex compounds, Mn(II) complexes of citric acid, ethylenediaminetetraacetic acid, or phosphoalkanepolycarboxylic acid are used.
6. Process in accordance with one of the claims 1-5, characterized in that mixtures of the Mn(II) compounds are used.
7. Process in accordance with the claims 1-6, characterized in that the manganese(II) compounds are used in a quantity of 0.01 to 5 g/l, especially 0.1 to 1 g/l and preferably 0.1 to 0.7 g/l.
8. Process in accordance with one of the claims 1-7, characterized in that a complexing agent is added to a dye bath containing an Mn(II) compound.
9. Process in accordance with one of the claims 1-8, characterized in that the dyeing is performed in the presence of a balancing auxiliary.
10. Process in accordance with one of the claims 1-8, characterized in that at least one manganese(II) compound is added to the bath during dyeing.
11. The polyamide fiber material obtained by the process in accordance with claim 1.
12. Process in accordance with one of the claims 1-9, characterized in that the manganese(II) compounds are applied to the fibers according to an extraction or continuous process.

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(57) Abstract

The invention pertains to a process for the dyeing of polyamide fiber mixtures which contain regularly stainable polyamide fiber materials and acid-modified polyamide fiber materials, with dye mixtures of acid dyes and cationic dyes, characterized in that before, during, or after the dyeing, at least one manganese(II) compound is added to the bath. The dyed materials obtained in this way show good light fastness.

DOCUMENTS CONSIDERED TO BE PERTINENT			
Category	Citation of document with indication if necessary of pertinent parts	claims	INT. CL. OF APPLICATION
A	EP 0 569 793 A (BAYER AG) *The entire document*	1	D06P 3/24, D06P 1/673, D06P 1/647, D06P 1/653, D06P 3/82, D06P 3/854 <u>Areas searched</u> D06P
E	DE 196 10 084 A (CIBA GEIGY AG) *The entire document*	1	
Location of search THE HAGUE		Date of search 18 Feb 1998	Examiner Heywood, C
<p>CATEGORY OF DOCUMENTS CITED</p> <p>X: especially pertinent alone</p> <p>Y: especially pertinent in combination with another document of same category</p> <p>A: technological background</p> <p>O: unwritten disclosure</p> <p>P: interim literature</p> <p>T: theory or principle at basis of invention</p> <p>E: older patent document only published on or after the application date</p> <p>D: document cited in the application</p> <p>L: document cited for other reasons</p> <p>& Member of same patent family, concordant document</p>			

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